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ORIGINAL PAPER

Use of the bond-projected superposition principle in determining the conditional probabilities of orbital events in molecular fragments

Roman F. Nalewajski

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Abstract The problem of defining and determining the *multi*-conditional probabilities of *many*-orbital events in the chemical bond system of a molecule is addressed anew within theoretical framework of the one-determinantal orbital representation of molecular electronic structure. Its solution is vital for determining the information-theoretic indices of bond couplings between molecular fragments or the reactant/product subsystems in chemical reactions. The superposition principle of quantum mechanics, appropriately projected into the occupied subspace of molecular orbitals, is used to condition the atomic orbitals or general basis functions of the self-consistent-field calculations. The conditional probabilities between the subspaces of basis functions (atomic orbitals) are derived from an appropriate generalization of the bond-projected superposition principle. They are then used to define the *triply*-conditional probabilities, relating one conditional event to another. The resulting expression is shown to satisfy the relevant *non*-negativity and symmetry requirements. It is applied to probe the π-bond coupling in butadiene and benzene.

Keywords Bond orders · Bond projections · Conditional probabilities of orbitals · Couplings of chemical bonds · Density matrix · Information theory · *Many*-orbital events · Molecular fragments · Molecular information channels · Orbital communication theory · Superposition principle for subspaces

Throughout the paper A denotes a *scalar* quantity, $\boldsymbol{A}$ stands for a *row-vector*, and $\mathbf{A}$ represents a square or rectangular matrix.

R. F. Nalewajski (✉)
Depatment of Theoretical Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland
e-mail: nalewajs@chemia.uj.edu.pl

1 Introduction

In the *Orbital Communication Theory* (OCT) of the chemical bond [1–5], which explores the information propagation in the orbitally-resolved molecular communication channels [6–9], the overall *information-theoretic* (IT) bond orders and their entropic covalent (communication "noise") and ionic (information "flow") components are generated from the appropriate conditional probabilities between *Atomic Orbitals* (AO) contributed by the system constituent atoms, generated by the bond-projected superposition principle of quantum mechanics [1–5,10]. The basis functions (AO) of the standard *Self-Consistent Field* (SCF) calculations determine a natural set of the elementary electron-occupation events within this orbital approximation of the molecular electronic structure. The ultimate goal of these orbital (Hartree-Fock or Kohn-Sham) theories is to determine the subspace of the occupied *Molecular Orbitals* (MO), which determine the system chemical bonds and the equilibrium (ground-state) distribution of electrons in molecules.

Recently, the Communication Theory of the Chemical Bond (CTCB) [1,6] has been extended to cover *many*-orbital events in the bond system of the molecule [1,3–5]. This development allows one to treat diverse bond-coupling phenomena between molecular fragments and reactant subsystems, which are often discussed in chemistry. For example, the alternative measures of the joint/conditional "probabilities" of the simultaneous *two*-orbital probability scatterings on different sites can be used to determine the IT-covalent and IT-ionic indices describing the mutual influences in the multi-site reactivity processes and catalysis, and it is capable of describing the coupling between the *inter*-reactant/product bonds in the concerted bond-forming/bond-weakening processes.

However, this promising *many*-orbital OCT perspective still suffers from several *non*-uniquenes and symmetry problems [1,3–5]. The previously designed, preliminary schemes within the superposition-principle approach, which have been used in the past to define the joint probabilities in the molecular bond system involving several AO, and the associated *multi*-conditional probabilities required to relate probability scatterings in different molecular fragments, still suffer from several shortcomings, e.g., *non*-positiveness and violation of some symmetries with respect to orbital exchanges. This hampers a wider use of the entropy/information descriptors they generate in interpreting subtle phenomena of the bond interactions in chemistry. It is the main purpose of this work to remedy this problem. The generalized superposition principle [1] for subspaces of basis functions, which closely follows the successful *two*-orbital development [2], will be shown to express the *triply*-conditional probabilities reflecting dependencies between information channels of molecular fragments in terms of elements of the molecular *first*-order density matrix.

2 *Two*-orbital probabilities in OCT

We begin with a short overview of the molecular communication systems in the AO/basis-function resolution and propagation of the condensed electron probabilities of AO in the molecular bond system [1,2]. The underlying conditional probabilities generate the entropy/information descriptors of the pattern of chemical bonds and their covalent and ionic composition in the molecular system under consideration. The conditional-entropy (communication noise) and mutual-information (information flow) descriptors of the molecular channel then provide the IT measures of the system covalency and ionicity, respectively [1,6].

Consider the standard *Restricted Hartree-Fock* (RHF) description of the molecular electronic structure, in which a network of chemical bonds between constituent atoms is determined by the occupied *Molecular Orbitals* (MO)$\boldsymbol{\varphi} = \{\varphi_s\}$ in the system ground-state. Assuming, for reasons of simplicity, the *closed*-shell configuration of $N = 2n$ electrons then identifies the n lowest (*doubly*-occupied, orthonormal) MO, $\boldsymbol{\varphi} = (\varphi_1, \varphi_2, \ldots, \varphi_n)$, as the origins of all bonds in the molecular system under consideration, both global (in the system as a whole) and regional (in molecular fragments). In the familiar LCAO MO approach MO are represented by the linear combinations $\boldsymbol{\varphi} = \boldsymbol{\chi}\mathbf{C}$ of the adopted orthonormal basis functions, $\boldsymbol{\chi} = (\chi_1, \chi_2, \ldots, \chi_m) = \{\chi_i\}$, $\langle \boldsymbol{\chi} | \boldsymbol{\chi} \rangle = \{\delta_{i,j}\} \equiv \mathbf{I}$, e.g., Löwdin's symmetrically orthogonalized AO; here, the rectangular matrix $\mathbf{C} = \left\{C_{i,s}\right\} = \langle \boldsymbol{\chi} | \boldsymbol{\varphi} \rangle$ groups the LCAO MO expansion coefficients, to be determined from the energy variational principle using the familiar *Self-Consistent Field* (SCF) procedure. The occupied MO thus determine the modes of the information propagation in the molecule, due to electron delocalization via the system chemical bonds.

The basis functions $\boldsymbol{\chi}$ define the underlying elementary "events" determining the channel *inputs* $\boldsymbol{a} = \{\chi_i\}$ and *outputs* $\boldsymbol{b} = \{\chi_j\}$, with the associated probabilities of finding an electron on these functions $\boldsymbol{P}(\boldsymbol{a}) = \{P(\chi_i) = p_i\} = \boldsymbol{p}$ and $\boldsymbol{P}(\boldsymbol{b}) = \{P(\chi_j) = q_j\} = \boldsymbol{q}$. The information network describing the orbital communications in the molecule is determined by the conditional probabilities of the channel outputs given inputs, $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{P(\chi_j|\chi_i) = P(j|i)\}$, $\sum_j P(j|i) = 1$. They describe the probability propagation via the system chemical bonds and are characterized by standard quantities developed in IT for real communication devices. The electron-delocalization in molecules via the system chemical bonds is embodied in the probability spread of each row $\{\boldsymbol{P}(\boldsymbol{b}|i)\}$ of $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a})$. In OCT these conditional probabilities follow from the quantum-mechanical superposition principle [10] supplemented by the "physical" projection of AO onto the subspace of the system occupied MO [1–5].

To summarize, the molecular information network in the AO resolution involves the full list of the AO-*events* $\boldsymbol{\chi}$ in its "*input*" $\boldsymbol{a} = \{\chi_i\}$ and "*output*" $\boldsymbol{b} = \{\chi_j\}$. It represents the effective communication promotion of these basis functions in the molecule, via the probability/information scattering described by the conditional probabilities of the AO-outputs given AO-inputs in the molecular bond system, identified by the *row* (input) and *column* (output) indices i and j, respectively. In OCT the entropy/information indicators of the covalent and ionic components of all chemical bonds in the given molecular system represent the complementary descriptors of the average communication-*noise* and information-*flow* in this molecular information channel.

In this orbital description the AO$\rightarrow$AO "communications" are thus fully characterized by the *conditional* probabilities $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \{P(i \wedge j)/P(i)\}$ of the output AO-events $\{\boldsymbol{b}\}$, given the input AO-events $(\boldsymbol{a})$, where the associated *joint* probabilities of simultaneously observing two AO in the system chemical bonds, $\mathbf{P}(\boldsymbol{a} \wedge \boldsymbol{b}) = \{P(i \wedge j)\}$, satisfy the usual normalizations:

$$\sum_i P(i \wedge j) = P(j), \quad \sum_j P(i \wedge j) = P(i), \quad \sum_i \sum_j P(i \wedge j) = 1. \tag{1}$$

The key quantity of the standard one-determinantal description is the *first*-order density matrix $\boldsymbol{\gamma}$ in the AO representation, also called the *Charge-and-Bond-Order* (CBO) matrix. It represents the projection operator onto the subspace of all (doubly occupied) MO, $\hat{\mathrm{P}}_{\boldsymbol{\varphi}} = |\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}| = \sum_s |\varphi_s\rangle\langle\varphi_s| \equiv \sum_s \hat{\mathrm{P}}_s$, $\hat{\mathrm{P}}_{\boldsymbol{\varphi}}^2 = \hat{\mathrm{P}}_{\boldsymbol{\varphi}}$,

$$\begin{aligned}\boldsymbol{\gamma} &= 2\langle\boldsymbol{\chi}|\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|\boldsymbol{\chi}\rangle = 2\mathbf{C}\mathbf{C}^{\dagger} \equiv 2\langle\boldsymbol{\chi}|\hat{\mathrm{P}}_{\boldsymbol{\varphi}}|\boldsymbol{\chi}\rangle \\ &= \left\{\gamma_{i,j} = 2\,\langle\chi_i|\,\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\,|\chi_j\rangle \equiv 2\,\langle i|\,\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\,|j\rangle \equiv 2\left\langle i^b|j^b\right\rangle\right\},\end{aligned} \tag{2}$$

where $\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\,|i\rangle = \left|i^b\right\rangle = |\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|i\rangle$ stands for the projection of χ_i onto the bond-subspace $\boldsymbol{\varphi}$, satisfying the associated closed-shell idempotency relation:

$$(\boldsymbol{\gamma})^2 = 4\langle\boldsymbol{\chi}|\hat{\mathrm{P}}_{\boldsymbol{\varphi}}|\boldsymbol{\chi}\rangle\langle\boldsymbol{\chi}|\hat{\mathrm{P}}_{\boldsymbol{\varphi}}|\boldsymbol{\chi}\rangle = 4\langle\boldsymbol{\chi}|\hat{\mathrm{P}}_{\boldsymbol{\varphi}}^2|\boldsymbol{\chi}\rangle = 4\langle\boldsymbol{\chi}|\hat{\mathrm{P}}_{\boldsymbol{\varphi}}|\boldsymbol{\chi}\rangle = 2\boldsymbol{\gamma}. \tag{3}$$

The CBO matrix reflects the promoted (valence) state of AO in the molecule. Its diagonal elements combine the effective electron occupations of the basis functions in the molecular ground-state, $\{N_i = \gamma_{i,i} = Np_i\}$, where $\boldsymbol{p} = \{p_i \equiv P(\chi_i) = \gamma_{i,i}/N\}$ stand for the (normalized) probabilities of AO being occupied in the molecule: $\sum_i p_i = N^{-1}\mathrm{Tr}\,\boldsymbol{\gamma} = 1$. This matrix also determines the system electron density,

$$\rho(\boldsymbol{r}) = 2\boldsymbol{\varphi}(\boldsymbol{r})\boldsymbol{\varphi}^{\dagger}(\boldsymbol{r}) = \boldsymbol{\chi}(\boldsymbol{r})\left[2\mathbf{C}\mathbf{C}^{\dagger}\right]\boldsymbol{\chi}^{\dagger}(\boldsymbol{r}) \equiv \boldsymbol{\chi}(\boldsymbol{r})\boldsymbol{\gamma}\boldsymbol{\chi}^{\dagger}(\boldsymbol{r}) = Np(\boldsymbol{r}), \tag{4}$$

and the *one*-electron probability distribution $p(\boldsymbol{r}) = \rho(\boldsymbol{r})/N$, the *shape* factor of ρ.

In quantum mechanics the *geometric* (g) conditional probability $P^g(\phi|\psi)$ of observing a normalized (variable) state, say ϕ, given another (parameter, reference) state, say ψ, emerges in the context of the superposition principle [10]:

$$P^g(\phi|\psi) = |\langle\psi|\phi\rangle|^2 = \langle\phi|\psi\rangle\langle\psi|\phi\rangle = \langle\phi|\hat{\mathrm{P}}_{\psi}|\phi\rangle = \langle\psi|\hat{\mathrm{P}}_{\phi}|\psi\rangle = P^g(\psi|\phi). \tag{5}$$

It should be observed that the quantum state conditioned upon itself in the molecular Hilbert space gives the probability of the sure event: $P^g(\psi|\psi) = 1$.

Since we are interested in the simultaneous AO events occurring in the bond system of the molecule the two scalar products in the preceding equations have to be calculated between the AO projections into the occupied subspace $\boldsymbol{\varphi}$ of MO [1,2]. Such *physical* conditional probabilities between AO are obtained by inserting the projector $\hat{\mathrm{P}}_{\boldsymbol{\varphi}}$ between the two states, say $\phi = \chi_j$ and $\psi = \chi_i$, involved in the two scalar products of the preceding geometrical expression:

$$\begin{aligned}P(j|i) &= \mathcal{N}_i|\langle i|\hat{\mathrm{P}}_{\boldsymbol{\varphi}}|j\rangle|^2 = \mathcal{N}_i\langle j|\hat{\mathrm{P}}_{\boldsymbol{\varphi}}|i\rangle\langle i|\hat{\mathrm{P}}_{\boldsymbol{\varphi}}|j\rangle = \mathcal{N}_i\langle j|\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\hat{\mathrm{P}}_i\hat{\mathrm{P}}_{\boldsymbol{\varphi}}|j\rangle \\ &\equiv \mathcal{N}_i\langle j|\hat{\mathrm{S}}_i|j\rangle = (2\gamma_{i,i})^{-1}\gamma_{i,j}\gamma_{j,i}\end{aligned} \tag{6}$$

This probability in thus determined as expectation value in the *final* state χ_j of the molecular scattering operator $\hat{\mathrm{S}}_i$ from the *initial* (reference) state χ_i:

$$\hat{\mathrm{S}}_i = \hat{\mathrm{P}}_{\boldsymbol{\varphi}}|i\rangle\langle i|\hat{\mathrm{P}}_{\boldsymbol{\varphi}} = \hat{\mathrm{P}}_{\boldsymbol{\varphi}}\ \hat{\mathrm{P}}_i\hat{\mathrm{P}}_{\boldsymbol{\varphi}} = |i^b\rangle\langle i^b|. \tag{7}$$

The proportionality constant $\mathcal{N}_i = (2\gamma_{i,i})^{-1}$ satisfies the required normalization condition [see Eq. 3]:

$$\sum_j P(j|i) = \mathcal{N}_i \sum_j \gamma_{i,j}\gamma_{j,i} = 2\mathcal{N}_i\gamma_{i,i} = 1.$$

Due to its dependence on the occupation $\gamma_{i,i}$ of the reference state χ_i in the molecular bond system the symmetry of Eq. 5 is observed only for equall effective occupations of both AO in the molecule.

One should also observe that for the identical AO in the conditioned pair,

$$P(i|i) = \gamma_{i,i}/2\ = 1/2\, Np_i. \tag{8}$$

This diagonal probability thus measures the number of electronic pairs on χ_i and reflects the probability p_i of this AO event in the molecule. This result correctly identifies the sure event of detecting electron on χ_i only for the double (full) occupation of this AO in the molecule, when $N_i = \gamma_{i,i} = 2$. This full orbital occupation also signifies that this AO does not participate in any chemical interactions with other orbitals, thus remaining purely *non*-bonded in character.

The *off*-diagonal conditional probability of jth AO-output given ith AO-input is thus proportional to the square of the CBO matrix element linking the two AO, which represents [see Eq. 2] the scalar product of the bond projections of two AO onto the bond subspace $\boldsymbol{\varphi}$. Therefore, this *two*-AO probability is also proportional to the corresponding contribution $\mathcal{M}_{i,j} = \gamma_{i,j}^2$ to the Wiberg [11] index of the chemical *bond*-order between the constituent atoms A and B in the molecule,

$$\mathcal{M}(\mathrm{A},\ \mathrm{B})\ = \sum_{i\in \mathrm{A}}\sum_{j\in \mathrm{B}} \mathcal{M}_{i,j}, \tag{9}$$

and to related *quadratic* descriptors of the molecular bond-multiplicities [12–21].

Using Eq. 3 it can be now readily verified that the associated matrix of the joint AO probabilities,

$$\mathbf{P}(\boldsymbol{a}\wedge\boldsymbol{b}) = \{P(i\wedge j) = P\,(i)\ P(j|i) = (2N)^{-1}\,\gamma_{i,j}\gamma_{j,i}\}, \tag{10}$$

satisfies the normalization conditions of Eq. 1, e.g.,

$$\sum_i P(i\wedge j)\ =\ (2N)^{-1}\sum_i \gamma_{j,i}\gamma_{i,j}\ =\ (2N)^{-1}\,2\gamma_{j,j} = P\,(j). \tag{11}$$

These relations also imply that molecular input probabilities $\boldsymbol{P}(\boldsymbol{a}) \equiv \boldsymbol{p}$ generate the same probabilities in the output of the molecular channel,

$$\boldsymbol{P}(\boldsymbol{b}) = \boldsymbol{p}\,\mathbf{P}(\boldsymbol{b}|\boldsymbol{a}) = \left\{\sum_i P(i)\,P(j|i) = \sum_i P(i \wedge j)\right\} = \boldsymbol{p}, \tag{12}$$

thus confirming the stationary character of this distribution.

The conditional probabilities of Eq. 6 explore the dependencies between AO resulting from their simultaneous participation in the system occupied MO, i.e., their involvement in the entire network of chemical bonds in the molecule. They define the probability scattering in the AO-channel of the molecule, in which the "signals" of the molecular/promolecular electron allocations to basis functions are transmitted from the AO inputs to AO outputs. Such information system constitutes the basis of OCT of the chemical bond [1–5]. This molecular channel can be probed using both the promolecular ($\boldsymbol{p}^0 = \{p_i^0\}$) and molecular ($\boldsymbol{p}$) input probabilities, in order to extract the IT-multiplicities of the *ionic* and *covalent* bond components, respectively. The atomic promolecule is defined by a collection of the "frozen" constituent (free) atoms brought to their final (molecular) locations. The AO probabilities $\boldsymbol{p}^0$ thus reflect the corresponding ground-states of the system separated atoms, which specify the initial state in the bond-formation process, in the spirit of the familiar *density*-difference function:

$$\Delta\rho(\boldsymbol{r}) = \rho(\boldsymbol{r}) - \rho^0(\boldsymbol{r}) = N[p(\boldsymbol{r}) - p^0(\boldsymbol{r})], \tag{13}$$

where $\rho^0(\boldsymbol{r})$ and $p^0(\boldsymbol{r}) = \rho^0(\boldsymbol{r})/N$ stand for the promolecular electron density and its shape/probability factor, respectively.

It should be emphasized that the elementary *geometrical* events $\{i\} = |\boldsymbol{\chi}\rangle$, of finding an electron on the specified basis functions $\{\chi_i\}$, e.g., the orthogonalized AO, correspond to the *pure* quantum states $\{|i\rangle\}$ identified by their individual projection operators $\{\hat{\mathrm{P}}_i = |i\rangle\langle i|\}$, with the whole basis-function space corresponding to the overall projection $\hat{\mathrm{P}}_{\boldsymbol{\chi}} = |\boldsymbol{\chi}\rangle\langle\boldsymbol{\chi}| = \sum_i \hat{\mathrm{P}}_i$. The *physical* events are conditional on the molecular ground state $|\psi\rangle$, approximated by a single Slater determinant defined by $|\boldsymbol{\varphi}\rangle = |\boldsymbol{\chi}\rangle\mathbf{C}$. Therefore, as indeed reflected by the MO-projected expression of Eq. 6, the AO events in the molecular bond system refer to the *mixed*-state reflected by the density operator:

$$\hat{\mathrm{D}}_{\boldsymbol{\chi}} = \frac{1}{2}\,|\boldsymbol{\chi}\rangle\,\boldsymbol{\gamma}\,\langle\boldsymbol{\chi}| = \frac{1}{2}\sum_i\sum_j |i\rangle\gamma_{i,j}\,\langle j| = \sum_i\sum_j \hat{\mathrm{P}}_i\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\hat{\mathrm{P}}_j. \tag{14}$$

This general observation, that elementary events are associated with the pure quantum states, i.e., with a single state vector in the molecular Hilbert space, while the conditional events correspond to the mixed quantum states, i.e., the ensembles defined by the relevant density operators, is essential for the *multi*-conditional development of Sect. 4, where we shall attempt to relate one conditional event upon another. Such probabilities should be thus associated with mixtures of the ensembles corresponding to the two conditional events in molecular subsystems.

3 Conditioning of orbital subspaces

It follows from Eq. 5 that the essence of the quantum conditioning of two states in $P^g(\phi|\psi)$, the expectation value in the variable state of the projector onto the parameter state, is the projection operator onto the reference state. This prescription is then supplemented in Eq. 6 by the additional projection onto the occupied subspace of MO, which reflects the actual participation of AO involved in the molecular chemical bond system. It is the main goal of this section to devise a similar procedure for conditioning the AO subspaces. In the next section we shall use this generalization to condition the *two*-AO scattering events on different molecular subsystems.

The same bond-projected superposition principle will now be used to derive these singly-conditional probabilities, which simultaneously involve larger subspaces of basis functions. Let us specifically examine the quantum conditioning of two subspaces in $\boldsymbol{\chi}$, spanned by the specified pairs of AO, each containing two basis functions: $\varepsilon_1 = \{\chi_i, \chi_j\} \equiv \{u(1)\}$ and $\varepsilon_2 = \{\chi_k, \chi_l\} \equiv \{w(2)\}$. These orbital pairs define the associated subspace projectors,

$$\hat{\mathrm{P}}_{\varepsilon_1} = |i\rangle\langle i| + |j\rangle\langle j| = \hat{\mathrm{P}}_i + \hat{\mathrm{P}}_j, \quad \hat{\mathrm{P}}_{\varepsilon_2} = |k\rangle\langle k| + |l\rangle\langle l| = \hat{\mathrm{P}}_k + \hat{\mathrm{P}}_l, \tag{15}$$

A natural generalization of the procedure adopted in the *two*-AO development of Eq. 6 calls for the trace over the variable subspace ε_1 of the projector onto the reference subspace ε_2. This gives the following *geometric* (g) expression, corresponding to the whole molecular Hilbert space,

$$\begin{aligned} P^g(\varepsilon_1|\varepsilon_2) &= \mathcal{N}^g \sum_{u(1)} \langle u(1)|\hat{\mathrm{P}}_{\varepsilon_2}|u(1)\rangle \\ &= \mathcal{N}^g \sum_{w(2)} \langle w(2)|\hat{\mathrm{P}}_{\varepsilon_1}|w(2)\rangle = P^g(\varepsilon_2|\varepsilon_1) \\ &= \mathcal{N}^g[\langle i|k\rangle\langle k|i\rangle + \langle i|l\rangle\langle l|i\rangle + \langle j|k\rangle\langle k|j\rangle + \langle j|l\rangle\langle l|j\rangle] \\ &= \mathcal{N}^g\left(\delta_{i,k} + \delta_{i,l} + \delta_{j,k} + \delta_{j,l}\right), \end{aligned} \tag{16}$$

where $\mathcal{N}^g$ denotes the appropriate normalization constant. Its *physical*, bond-projected analog then reads:

$$\begin{aligned} P(\varepsilon_1|\varepsilon_2) &= \mathcal{N}_2 \sum_{u(1)} \langle u(1)|\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\hat{\mathrm{P}}_{\varepsilon_2}\hat{\mathrm{P}}_{\boldsymbol{\varphi}}|u(1)\rangle \equiv \mathcal{N}_2 \mathrm{Tr}_{\varepsilon_1}\hat{\mathrm{S}}_{\varepsilon_2} \\ &= \mathcal{N}_2\left(\gamma_{i,k}\gamma_{k,i} + \gamma_{i,l}\gamma_{l,i} + \gamma_{j,k}\gamma_{k,j} + \gamma_{j,l}\gamma_{l,j}\right) \\ &= \mathcal{N}_2\left[(\gamma_{i,k})^2 + (\gamma_{i,l})^2 + (\gamma_{j,k})^2 + (\gamma_{j,l})^2\right] \geq 0, \end{aligned} \tag{17}$$

where the probability scattering operator from the reference subspace [compare Eq. 7]

$$\hat{\mathrm{S}}_{\varepsilon_2} = \hat{\mathrm{P}}_{\boldsymbol{\varphi}}\hat{\mathrm{P}}_{\varepsilon_2}\hat{\mathrm{P}}_{\boldsymbol{\varphi}} \equiv \hat{\mathrm{P}}_{\varepsilon_2^b} = \sum_{w\in\varepsilon_2} |w^b\rangle\langle w^b|. \tag{18}$$

As required, the resulting expression for the *non*-negative conditional probability $P(\varepsilon_1|\varepsilon_2)$ is seen to be symmetrical with respect to exchanges of orbitals inside and between the two subspaces. It combines the (renormalized) additive *two*-orbital contribution for all selections of single orbitals in the variable and parameter subspaces, respectively. It is straightforward to calculate once the self-consistent density matrix is known. This result can be extended to cover any number of basis functions in each subspace. Such conditional probabilities reflect communications between members of the two spaces involved and generate the associated IT covalent and ionic descriptors of the collective chemical interactions between these groups of orbitals in the molecular ground-state.

Again, the proportionality constant $\mathcal{N}_2$ has to satisfy the relevant normalization condition, the sum rule over all admissible selections of AO-pairs in the dependent set ε_1:

$$\mathrm{tr}_{\{\varepsilon(i,j)\}}P(i,j\,|k,l) = 1; \tag{19}$$

here $\mathrm{tr}_{\{\varepsilon(i,j)\}} = \mathrm{tr}_{\cup\{(i,j)\}} = \mathrm{tr}_{\boldsymbol{\varphi}}$ denotes the trace over the union of all *double*-AO subspaces in the molecular bond space spanned by the orthogonal MO $|\boldsymbol{\varphi}\rangle$, for all selections of both AO indices. The resulting subspace exhausts the whole bond space itself, determined also by the *non*-orthogonal bond-projections $|\boldsymbol{\chi}^b\rangle$ of all basis functions. Indeed, since only electrons carry the physical information in the molecule, the preceding equation expresses the fact that the signal originating from the subspace $\varepsilon_2 = \{\chi_k, \chi_l\}$ will be *totally* scattered inside the bonding space of the doubly occupied MO,

$$\sum_{\varepsilon_1}\hat{\mathrm{P}}_{\varepsilon_1^b} = \hat{\mathrm{P}}_{\boldsymbol{\varphi}} = \hat{\mathrm{P}}_{\boldsymbol{\chi}^b} = \sum_i |i^b\rangle\langle i^b|. \tag{20}$$

Therefore, the overall normalization is expressed by the trace over the whole bonding space, which amounts to a single sumation over the repeated index of products of CBO matrix elements of any of the basis functions of $\varepsilon(i,j)$ in Eq. 17:

$$\begin{aligned}\mathrm{tr}_{\{\varepsilon(i,j)\}}(\gamma_{k,i}\gamma_{i,k} + \gamma_{i,l}\gamma_{l,i} + \gamma_{j,k}\gamma_{k,j} + \gamma_{j,l}\gamma_{l,j}) &\equiv \sum_i(\gamma_{i,k}\gamma_{k,i} + \gamma_{l,i}\gamma_{i,l}) \\ &\quad + \sum_j(\gamma_{k,j}\gamma_{j,k} + \gamma_{l,j}\gamma_{j,l}) \\ &= 4(\gamma_{k,k} + \gamma_{l,l}).\end{aligned} \tag{21}$$

Finally, the normalization condition of Eq. 19 reads:

$$\mathcal{N}_2\mathrm{tr}_{\boldsymbol{\varphi}}\hat{\mathrm{S}}_{\varepsilon_2} = \mathcal{N}_2 4\left(\gamma_{k,k} + \gamma_{l,l}\right) = 1, \tag{22}$$

and hence $\mathcal{N}_2 = 1/[4(\gamma_{k,k} + \gamma_{l,l})]$.

The final expression for the *singly*-conditional probability relating in the bond space one *two*-AO subspace to another *two*-AO subspace,

$$P(i, j|k, l) = [4(\gamma_{k,k} + \gamma_{l,l})]^{-1}(\gamma_{i,k}\gamma_{k,i} + \gamma_{i,l}\gamma_{l,i} + \gamma_{j,k}\gamma_{k,j} + \gamma_{j,l}\gamma_{l,j}), \quad (23)$$

constitutes a natural generalization of the *two*-AO expression of Eq. 6. As expected this probability vanishes when there is no chemical coupling between the two AO-subsets, $\gamma_{i,k} = \gamma_{i,l} = \gamma_{j,k} = \gamma_{j,l} = 0$, either because of the symmetry requirements or due to their large spatial separation $R_{1,2} \rightarrow \infty$:

$$P(i, j|k, l) \rightarrow 0\,(R_{1,2} \rightarrow \infty). \quad (24)$$

This probability is seen to assume a general form of the known *two*-orbital expression of Eq. 6,

$$P(\varepsilon_1|\varepsilon_2) = \gamma^2_{\varepsilon_1,\varepsilon_2}/\left(2\gamma_{\varepsilon_2,\varepsilon_2}\right), \quad (25)$$

when expressed in terms of the *average* "chemical" coupling $\gamma_{\varepsilon_1,\varepsilon_2}$ between the two conditioned subspaces,

$$\gamma^2_{\varepsilon_1,\varepsilon_2} = 1/4\left[(\gamma_{i,k})^2 + (\gamma_{i,l})^2 + (\gamma_{j,k})^2 + (\gamma_{j,l})^2\right], \quad (26)$$

and the average AO electron occupation in the parameter subspace,

$$\gamma_{\varepsilon_2,\varepsilon_2} = \frac{1}{2}(\gamma_{k,k} + \gamma_{l,l}). \quad (27)$$

This conditional probability also defines the associated *joint*-probability of the two subspaces in the bonding space of the molecule:

$$\begin{aligned} P[(i, j) \wedge (k, l)] &\equiv P(k \wedge l)P(i, j|k, l) \\ &= [8N(\gamma_{k,k} + \gamma_{l,l})]^{-1}(\gamma_{k,l})^2\left[(\gamma_{i,k})^2 + (\gamma_{i,l})^2\right. \\ &\quad \left. + (\gamma_{j,k})^2 + (\gamma_{j,l})^2\right], \end{aligned} \quad (28)$$

which also conforms to the adopted normalization over the union of all admissible *two*-AO subspaces:

$$\begin{aligned} \mathrm{tr}_{\{\varepsilon(i,j)\}} P[(i, j) \wedge (k, l)] &= [8N(\gamma_{k,k} + \gamma_{l,l})]^{-1}(\gamma_{k,l})^2 4(\gamma_{k,k} + \gamma_{l,l}) \\ &= (\gamma_{k,l})^2/(2N) = P(k \wedge l) \equiv P(k, l). \end{aligned} \quad (29)$$

4 Conditioning of probability propagations in molecular fragments

Let us now address the associated problem of conditioning the probability propagations in molecular fragments. In communication theory the localized chemical interaction between the given pair $\{\chi_i, \chi_j\}$ of AO reflects the probability scattering between these two basis functions. It is embodied in the respective elements $P(j|i)$ and $P(i|j)$ of the conditional probability matrix $\mathbf{P}(\boldsymbol{b}|\boldsymbol{a})$. In order to quantify in IT the coupling effects between such localized chemical bonds, say between χ_i and χ_j in one molecular fragment, and between χ_k and χ_l in another part of the molecule, when $\varepsilon_1 = (\chi_i, \chi_j)$ and $\varepsilon_2 = (\chi_k, \chi_l)$ are disjoint, one has to relate the two conditional events $\alpha = (j|i)$ and $\beta = (l|k)$ in both these subsystems. One thus requires the *triply*-conditional probability $P[(j|i)|(l|k)]$, of the *variable* (conditional) *two*-orbital event (in one fragment, of the $i \to j$ scattering, conditional on the *parameter* (conditional) *two*-orbital event in another fragment, of the $k \to l$ probability propagation. Clearly, the AO labels in each subspace and in both conditional events may be repeated, to account for the *intra*-subsystem bond contributions.

Earlier attempts [1,5] to solve a seemingly *non*-unique problem of generating such propagation-coupling, *triply*-conditional probabilities $P[(i|j)|(k|l)]$ and the associated joint probabilities $P[(i|j) \wedge (k|l)] = P[(i|j)|(k|l)]P(k|l) \equiv P[(i|j), (k|l)]$, was shown to violate the requirements of the *non*-negativity and of relevant symmetries with respect to exchange of orbitals, although for equal AO occupations they satisfy Bayes' rule,

$$P(\beta|\alpha) = P(\beta)P(\alpha|\beta)/P(\alpha) = P(\beta)P(\alpha|\beta)/\Big[\sum_{\beta} P(\beta)P(\alpha|\beta)\Big], \tag{30}$$

about "hypotheses" $\{\beta\}$ accounting for the occurrence of α. Its first part implies that the probability ratio of individual propagations can be expressed as the corresponding ratio of their reverse conditional probabilities:

$$P(\beta)/P(\alpha) = P(\beta|\alpha)/P(\alpha|\beta). \tag{31}$$

The underlying joint probabilities of the simultaneous *four*-orbital events in the molecular bond space, $P[(i \wedge j) \wedge (k \wedge l)] \equiv P(i, j, k, l)$, originate from the AO participation in the system ground-state. As we have already recognized above, the conditioning of χ_j on χ_i amounts to the projection upon the variable orbital χ_j on the reference orbital χ_i in the bonding subspace of MO. This operation is effected by the scattering operator $\hat{\mathrm{S}}_i$. The subspace generalization of this procedure, involving a trace over one *bond*-subspace of the projection onto another *bond*-subspace, similarly generates the *singly*-conditional probability $P(\varepsilon_1|\varepsilon_2)$. The *triply*-conditional probabilities $P[(j|i)|(l|k)]$ can thus be viewed as being derived from a sequence of such three conditioning operations $\hat{\mathrm{C}}(\zeta\,|\xi\,)$ performed on molecular basis functions, where ζ and ξ denote either a single AO's or their pairs $\varepsilon_1 = (i, j)$ and $\varepsilon_2 = (k, l)$: two operations $\hat{\mathrm{C}}(j\,|i\,)$and $\hat{\mathrm{C}}(l\,|k\,)$ conditioning a pair of orbitals in each set, and the subspace-conditiong $\hat{\mathrm{C}}(\varepsilon_1\,|\varepsilon_2\,)$.

For example, one can view the probability $P[(j|i)|(l|k)]$ as resulting from $P(\varepsilon_1|\varepsilon_2)$ by the extra-conditioning performed within each of the *two*-AO subspaces: $\hat{\mathrm{C}}(j\,|i\,)\hat{\mathrm{C}}(l\,|k\,)\hat{\mathrm{C}}(\varepsilon_1\,|\varepsilon_2\,)$. Alternatively, one can start from two conditional events in each of these subspaces, with probabilities $P(j|i)$ and $P(l|k)$, respectively, with subsequent conditioning of the two subspaces themselves: $\hat{\mathrm{C}}(\varepsilon_1\,|\varepsilon_2\,)\hat{\mathrm{C}}(j\,|i\,)\hat{\mathrm{C}}(l\,|k\,)$. These operations do not commute, however, with each scheme leading to *non*-negative though different expressions for $P[(j|i)|(l|k)]$, $P[(i|j),\,(k|l)]$ and $P(i,\,j,\,k,\,l)$. The resulting expressions also fail to satisfy the Bayes rule.

Consider a particular example of the first of these conditioning sequences. As we have already recognized in Eq. 6, the conditioning within a given pair of AO amounts to the projection upon the reference orbital in the bonding subspace of MO. This operation is effected by the scattering operator $\hat{\mathrm{S}}_i$ [Eq. 7]. The *triply*- conditional probabilities $P[(j|i)|(l|k)]$ can now be viewed as derived from the subspace probability $P(\varepsilon_1|\varepsilon_2)$ [Eq. 17], where such extra-conditioning has been performed within each of the *two*-AO subspaces, since now both events to be conditioned are already conditional themselves. However, since the reference orbital χ_i in $[(j|i)|(l|k)]$ belongs to the variable subspace ε_1 the trace of Eq. 17 should now be performed over the $\hat{\mathrm{S}}_i$ projected subspace

$$\varepsilon_1^{(i)} \equiv \hat{\mathrm{S}}_i\varepsilon_1 = \left(\hat{\mathrm{S}}_i\,|i\rangle\,,\,\hat{\mathrm{S}}_i\,|j\rangle\right) = |\boldsymbol{\varphi}\rangle\,\langle\boldsymbol{\varphi}|\ i\rangle\,(\gamma_{i,i},\gamma_{i,j}) \equiv \left|i^b\right\rangle(\gamma_{i,i},\gamma_{i,j}). \tag{32}$$

Similarly, since the other reference orbital χ_k in $[(j|i)|(l|k)]$ is a member of the reference subspace ε_2 the projection $\hat{\mathrm{S}}_k$ should now be performed on the operator part of Eq. 17:

$$\hat{\mathrm{S}}_{\varepsilon_2}^{(k)} \equiv \hat{\mathrm{S}}_k\hat{\mathrm{S}}_{\varepsilon_2}\hat{\mathrm{S}}_k = \hat{\mathrm{P}}_{\boldsymbol{\varphi}}\hat{\mathrm{P}}_k\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\left(\hat{\mathrm{P}}_k+\hat{\mathrm{P}}_l\right)\hat{\mathrm{P}}_{\boldsymbol{\varphi}}\hat{\mathrm{P}}_k\hat{\mathrm{P}}_{\boldsymbol{\varphi}}. \tag{33}$$

This procedure finally gives:

$$\begin{aligned} P[(j|i)|(l|k)] &= \mathscr{N}\mathrm{Tr}_{\varepsilon_1^{(i)}}\hat{\mathrm{S}}_{\varepsilon_2}^{(k)} \\ &= \mathscr{N}(\gamma_{i,k})^2\left[(\gamma_{i,i})^2+(\gamma_{i,j})^2\right]\left[(\gamma_{k,k})^2+(\gamma_{k,l})^2\right]\geq 0, \end{aligned} \tag{34}$$

where $\mathscr{N}$ stands for the appropriate normalization constant.

It also follows from Eq. 23 that the projected subspace $\varepsilon_1^{(i)}$ contains two pieces of the bond-projection $|i^b\rangle = |\boldsymbol{\varphi}\rangle\langle\boldsymbol{\varphi}|i\rangle$ of orbital χ_i, which determines the orbital electron occupation $\gamma_{i,i} = 2\left\langle i^b|i^b\right\rangle$. Together they give rise to the overall norm

$$\mathscr{N}\left[\varepsilon_1^{(i)}\right] = 1/2\,\gamma_{i,i}\left[(\gamma_{i,i})^2+(\gamma_{i,j})^2\right], \tag{35}$$

given by the the trace of the subspace metric tensor:

$$\left\langle\varepsilon_1^{(i)}\left|\varepsilon_1^{(i)}\right.\right\rangle = \left\langle i^b\middle|i^b\right\rangle\begin{bmatrix}\gamma_{i,i}^2 & \gamma_{i,i}\gamma_{i,j}\\ \gamma_{i,j}\gamma_{i,i} & \gamma_{i,j}^2\end{bmatrix} = \frac{\gamma_{i,i}}{2}\begin{bmatrix}\gamma_{i,i}^2 & \gamma_{i,i}\gamma_{i,j}\\ \gamma_{i,j}\gamma_{i,i} & \gamma_{i,j}^2\end{bmatrix}. \tag{36}$$

When the two conditional events are interchanged, the associated norm of $\varepsilon_2^{(k)}$,

$$\mathcal{N}\big[\varepsilon_2^{(k)}\big] = 1/2\,\gamma_{k,k}\left[(\gamma_{k,k})^2 + (\gamma_{k,l})^2\right], \tag{37}$$

measures the trace of the associated bond-projected metric tensor

$$\left\langle \varepsilon_2^{(k)} \middle| \varepsilon_2^{(k)} \right\rangle = \langle k^b | k^b \rangle \begin{bmatrix} \gamma_{k,k}^2 & \gamma_{k,k}\gamma_{k,l} \\ \gamma_{k,l}\gamma_{k,k} & \gamma_{k,l}^2 \end{bmatrix} = \frac{\gamma_{k,k}}{2} \begin{bmatrix} \gamma_{k,k}^2 & \gamma_{k,k}\gamma_{k,l} \\ \gamma_{k,l}\gamma_{k,k} & \gamma_{k,l}^2 \end{bmatrix}. \tag{38}$$

Therefore, it follows from Eqs. 35 and 37 that the *triply*-conditional probability of Eq. 34 is proportional to the above norms of the conditional subspaces:

$$P[(j|i)|(l|k)] = \{4\mathcal{N}(\gamma_{i,k})^2/(\gamma_{i,i}\gamma_{k,k})\}\mathcal{N}\big[\varepsilon_1^{(i)}\big]\mathcal{N}\big[\varepsilon_2^{(k)}\big]. \tag{39}$$

Finally, one can fix the normalization of such *triply*-conditional probability measures by the admissible requirement:

$$P[(j|i)|(j|i)] = P(j|i). \tag{40}$$

In the spirit of Eq. 8 it relates this *pair*-diagonal, *triply*-conditional probability, of the (conditional) *two*-AO event conditional upon itself, to the probability of the conditional event itself. This equation gives the normalization constant,

$$\mathcal{N} = \gamma_{i,j}^2 \Big/ \left[2\gamma_{i,i}^3\left(\gamma_{i,i}^2 + \gamma_{i,j}^2\right)^2\right], \tag{41}$$

and hence the final expression for the *triply*-conditional probability:

$$P[(j|i)|(l|k)] = P(\alpha|\beta) = \frac{\gamma_{i,j}^2\gamma_{i,k}^2\left(\gamma_{k,k}^2 + \gamma_{k,l}^2\right)}{2\gamma_{i,i}^3\left(\gamma_{i,i}^2 + \gamma_{i,j}^2\right)} \geq 0. \tag{42}$$

This form clearly distinguishes between the variable $(j|i)$ and parameter $(l|k)$ *two* orbital events. It also implies that a nonvanishing probability for the occupied AO, $\gamma_{i,i} > 0$, requires the finite coupling between the reference orbitals of two subspaces, through $\gamma_{i,k} \neq 0$, and the chemical interaction between the two orbitals in the variable subspace: $\gamma_{i,j} \neq 0$. This accords with the intuitive expectation that conditioning of the electron scattering events (chemical bonds) on molecular fragments requires the chemical interactions between these subsystems.

It should be observed however, that the associated measure of the joint probability of the simultaneous occurrence of the two conditional events:

$$P[(j|i),\ (l|k)] = P(l|k)P[(j|i)|(l|k)] = \frac{\gamma_{i,j}^4\gamma_{i,k}^2(\gamma_{k,k}^2 + \gamma_{k,l}^2)}{4\gamma_{i,i}^4(\gamma_{i,i}^2 + \gamma_{i,j}^2)} \geq 0, \tag{43}$$

still fails to satisfy the symmetry requirement with respect to exchange $\alpha \equiv (j|i) \leftrightarrow (l|k) \equiv \beta$.

In designing the *fully symmetrical* measure of these triply conditional probabilities of AO events in the molecular bond system one can also follow the heuristic approach of Eqs. 25–27:

$$P(\alpha|\beta) = \gamma_{\alpha,\beta}^2 / \left(2\gamma_{\beta,\beta}\right), \tag{44}$$

where $\gamma_{\alpha,\beta}$ denotes the appropriate average chemical interaction attributed to two conditional AO events α and β, and $\gamma_{\beta,\beta}$ stands for the effective electron occupation associated with the reference conditional event. In order to determine these quantities we use the known probabilities of the separate events α and β, applied as weighting factors,

$$\gamma_{\alpha,\beta}^2 = P(\alpha)\gamma_{\varepsilon_1,\varepsilon_2}^2 P(\beta), \quad \gamma_{\beta,\beta} = P(\beta)\gamma_{\varepsilon_2,\varepsilon_2}. \tag{45}$$

The emerging heuristic expression for the triply conditional probabilities then reads:

$$\begin{aligned} P(\alpha|\beta) &= P(\alpha)\gamma_{\varepsilon_1,\varepsilon_2}^2/(2\gamma_{\varepsilon_2,\varepsilon_2}) \\ &= \left\{(\gamma_{i,j})^2[4\gamma_{i,i}(\gamma_{k,k}+\gamma_{l,l})]^{-1}\right\}\left[(\gamma_{i,k})^2+(\gamma_{i,l})^2+(\gamma_{j,k})^2+(\gamma_{j,l})^2\right]. \end{aligned} \tag{46}$$

The crucial test of its adequacy comes from calculating Bayes' ratio of Eq. 31:

$$P(\beta|\alpha)/P(\alpha|\beta) = (\gamma_{k,l})^2\gamma_{i,i}(\gamma_{k,k}+\gamma_{l,l})/[(\gamma_{i,j})^2\gamma_{k,k}(\gamma_{i,i}+\gamma_{j,j})], \tag{47}$$

to be compared with the probability ratio of individual conditional events:

$$P(\beta)/P(\alpha) = (\gamma_{k,l})^2\gamma_{i,i}/\left[(\gamma_{i,j})^2\gamma_{k,k}\right]. \tag{48}$$

One observes that the symmetrical expression of Eq. 46 indeed satisfies Bayes' rule for equal occupations of the two orbital subspaces:

$$N_{\varepsilon_1} = \gamma_{i,i}+\gamma_{j,j} = 2\gamma_{\varepsilon_1,\varepsilon_1} = N_{\varepsilon_2} = \gamma_{k,k}+\gamma_{l,l} = 2\gamma_{\varepsilon_2,\varepsilon_2}. \tag{49}$$

We can thus conclude that this probability can serve as another adequate measure of the propagation-coupling probabilities which emerge in the *bond*-coupling phenomena of OCT.

The additional test comes from the symmetry requirement of the resultant joint probabilities of the two conditional events:

$$P(\alpha \wedge \beta) = P(\beta)P(\alpha|\beta) = P(\alpha)P(\beta|\alpha). \tag{50}$$

The two probability products respectively give:

$$
\begin{aligned}
P(\beta)P(\alpha|\beta) &= P(\alpha)\gamma^2_{\varepsilon_1,\varepsilon_2}P(\beta)/(2\gamma_{\varepsilon_2,\varepsilon_2}) = \gamma^2_{\alpha,\beta}/N_{\varepsilon_2} \quad \text{and} \\
P(\alpha)P(\beta|\alpha) &= P(\alpha)\gamma^2_{\varepsilon_1,\varepsilon_2}P(\beta)/(2\gamma_{\varepsilon_1,\varepsilon_1}) = \gamma^2_{\alpha,\beta}/N_{\varepsilon_1}.
\end{aligned} \tag{51}
$$

These probabilities are indeed equal for equal occupations of the two orbital subspaces. In practical molecular calculations the average of these two estimates should be used as the fully symmetrical *joint*-probability measure:

$$
\begin{aligned}
P(\alpha \wedge \beta) &= 1/2\,[P(\beta)P(\alpha|\beta) + P(\alpha)P(\beta|\alpha)] \\
&= 1/2\,\gamma^2_{\alpha,\beta}[1/N_{\varepsilon_1} + 1/N_{\varepsilon_2}] \equiv \frac{\gamma^2_{\alpha,\beta}}{2N^h_{(\varepsilon_1,\varepsilon_2)}},
\end{aligned} \tag{52}
$$

which assumes a general form of the *two*-orbital expression of Eq. 10 when expressed in terms of the harmonic average $N^h_{(\varepsilon_1,\varepsilon_2)}$ of the two subspace occupations.

This expression approximately satisfies the associated normalization requirements for joint probabilities,

$$
\begin{aligned}
\sum_\alpha P(\alpha \wedge \beta) &= \left[2N^h_{(\varepsilon_1,\varepsilon_2)}\right]^{-1} \sum_\alpha \gamma^2_{\alpha,\beta} \\
&= \left[2N^h_{(\varepsilon_1,\varepsilon_2)}\right]^{-1} \left[\sum_\alpha P(\alpha)\right]\left[\mathrm{tr}_{\{\varepsilon_1\}}\gamma^2_{\varepsilon_1,\varepsilon_2}\right] P(\beta) \\
&= \left[N_{\varepsilon_2}/2N^h_{(\varepsilon_1,\varepsilon_2)}\right] P(\beta) \approx \; P(\beta),
\end{aligned} \tag{53}
$$

for equal electron occupations of the two subspaces, when $N_{\varepsilon_2} = 2N^h_{(\varepsilon_1,\varepsilon_2)}$.

5 Illustrative application to π-electron systems

The preliminary approach to *multi*-conditional events of π-electrons in butadiene and benzene have recently been discussed using the Hückel CBO data [5]. Since the *bond*-projected, coupling measure of the *many*-AO "probabilities" adopted in this study exhibited several shortcomings, it is of interest to reexamine this interesting chemical problem using the present *multi*-bond probabilities generated by Eqs. 42 and 47, derived from the bond-projected superposition principle for subspaces of basis functions, which are free of some of these fundamental deficiencies. In what follows we shall apply the ground-state density matrices reported in ref. [5] for butadiene and benzene, for the consecutive numbering of the $2p_\pi$ orbitals contributed by the constituent carbon atoms.

Let us first examine predictions from Eq. 42. For butadiene the present approach gives the following (symmetry-unrelated) *pair*-diagonal probabilities involving different AO:

$$
\begin{aligned}
&P[(1|2)|(1|2)] = P(1|2) = 0.40,\\
&P[(1|4)|(1|4)] = P(1|4) = P[(2|3)|(2|3)] = P(2|3) = 0.10,\\
&P[(1|3)|(1|3)] = P(1|3) = 0.00.
\end{aligned} \tag{54a}
$$

They reflect differences between the strong information couplings of the probability scatterings in the peripheral 1–2 (3–4) π bonds, a weaker chemical interaction inside the middle 2–3 bond and the 1–4 "bond" connecting peripheral atoms, and the absence of any interaction between "bonds" connecting the chemically *non*-bonded pairs of atoms: 1–3 (2–4).

Using Eq. 42 one similarly finds the representative probabilities for the *pair*-non-diagonal events in the π-electron system of butadiene:

$$
\begin{aligned}
&P[(1|1)|(2|1)] = 0.45, \quad P[(1|1)|(4|1)] = 0.30, \quad P[(1|1)|(3|1)] = 0.25,\\
&P[(1|2)|(3|2)] = 0.27, \quad P[(1|2)|(4|1)] = P[(1|2)|(2|3)] = 0.21,\\
&P[(1|2)|(3|1)] = 0.18, \quad P[(1|4)|(2|3)] = P[(1|2)|(4|3)] = 0.08,\\
&P[(1|2)|(1|3)] = 0.04,\\
&P[(1|2)|(1|4)] = P[(1|2)|(3|4)] = P[(1|3)|(3|4)] = 0.00.
\end{aligned} \tag{55a}
$$

The vanishing *non*-diagonal probabilities, in the last row of the preceding equation, are due to the absence of the chemical interaction between the two reference orbitals ($\gamma_{i,k} = 0$) and/or in the variable subspace ($\gamma_{i,j} = 0$) in the symbol of the *triple*-conditional event. The preceding, *non*-vanishing probabilities correctly reflect the expected strength of the inter-bond probability scatterings involving neighboring and more distant atoms, the peripheral and middle bonds, and they correctly reflect a lesser weight of the probability scattering between non-bonded atoms.

The corresponding pair-diagonal probabilities for benzene reflect the strength of chemical π bonds in the regular-hexagon ring of carbon atoms:

$$
\begin{aligned}
&P[(i|i)|(i|i)] = P(i|i) = 0.50, \quad P[(i+1|i)|(i+1|i)] = P(i+1|i) = 0.22,\\
&P[(i+2|i)|(i+2|i)] = P(i+2|i) = 0.00,\\
&P[(i+3|i)|(i+3|i)] = P(i+3|i) = 0.06.
\end{aligned} \tag{56a}
$$

The representative *pair*-non-diagonal probabilities coupling two different π bonds in the benzene ring read:

$$
\begin{aligned}
&P[(i|i)|(i+1|i)] = 0.36, \quad P[(i|i)|(i+2|i)] = 0.25,\\
&P[(i|i)|(i+3|i)] = 0.28, \quad P[(i|i)|(i+2|i+1)] = 0.16,\\
&P[(i|i)|(i+3|i+2)] = P[(i+1|i)|(i+3|i+2)] = 0.00,\\
&P[(i+1|i)|(i+2|i+1)] = 0.10, \quad P[(i+1|i)|(i+4|i+3)] = 0.02.
\end{aligned} \tag{57a}
$$

Again, these probabilities adequately reflect both the spatial separation of both the two atoms in each pair and the pair-separation in the benzene ring, as well as the chemical interactions between the constituent carbon atoms quantified by the respective bond-orders.

Next, let us summarize the corresponding *propagation*-coupling predictions from the most symmetrical Eq. 47, which was shown to be heuristically related to the singly/conditional probabilities and to satisfy Bayes's hypotheses relations. For butadiene one obtains the following triply/conditional probabilities:

$$\begin{aligned} &P[(1|2)|(1|2)] = 0.36, \quad P[(1|4)|(1|4)] = P[(2|3)|(2|3)] = 0.06, \\ &P[(1|3)|(1|3)] = 0.00; \end{aligned} \tag{54b}$$

$$\begin{aligned} &P[(1|1)|(2|1)] = 0.45, \quad P[(1|1)|(4|1)] = 0.30, \quad P[(1|1)|(3|1)] = 0.25, \\ &P[(1|2)|(3|2)] = P[(1|2)|(4|1)] = P[(1|2)|(2|3)] = P[(1|2)|(3|1)] = 0.20, \\ &P[(1|4)|(2|3)] = P[(1|2)|(4|3)] = 0.04, \quad P[(1|2)|(3|4)] = 0.04, \\ &P[(1|2)|(1|3)] = P[(1|2)|(1|4)] = 0.20, \quad P[(1|3)|(3|4)] = 0.00. \end{aligned} \tag{55b}$$

The corresponding heuristic probabilities for benzene read:

$$\begin{aligned} &P[(i|i)|(i|i)] = 0.50, \quad P[(i+1|i)|(i+1|i)] = P(i+1|i) = 0.16, \\ &P[(i+2|i)|(i+2|i)] = 0.00, \quad P[(i+3|i)|(i+3|i)] = P(i+3|i) = 0.03; \end{aligned} \tag{56b}$$

$$\begin{aligned} &P[(i|i)|(i+1|i)] = 0.36, \quad P[(i|i)|(i+2|i)] = 0.25, \quad P[(i|i)|(i+3|i)] = 0.28, \\ &P[(i|i)|(i+2|i+1)] = 0.11, \quad P[(i|i)|(i+3|i+2)] = 0.03, \\ &P[(i+1|i)|(i+3|i+2)] = 0.09, \\ &P[(i+1|i)|(i+2|i+1)] = 0.10, \quad P[(i+1|i)|(i+4|i+3)] = 0.01. \end{aligned} \tag{57b}$$

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